Development of Cost-Effective Ceramic and Refractory Components for Aluminum Melting and Casting

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Outline

- Issues
- Objective of research
- Research tasks
- Research / milestones completed
  - Microstructural characterization
  - Wetting and reactivity studies
  - Permeability
  - Glazes
  - Particle size distribution
- Near term future work / milestones

Issues

- Reaction of constituents in refractory materials with molten aluminum limits the useful life of refractory components.

- Permeability of ceramic/refractory products inhibits their ability to perform in casting applications requiring pressurization.

Objective

- Develop and validate new classes of cost-effective low-permeability ceramic and refractory components for handling molten aluminum in both smelting and casting environments
- Develop materials and methods for sealing surface porosity in thermal shock-resistant ceramic refractories
- Optimize refractory formulations to minimize wetting by molten aluminum, and characterize erosion, corrosion, and spallation rates under realistic service conditions.
- Scale up the processing methods to full-sized components and field test in commercial aluminum casting shops.

Outcome of the Improved Material

- Reduced downtime through longer life
- Reduction in scrap through lower rates of erosion and particulate generation
- Reduction in the overall energy use by improving casting operations
- Enhancement in the performance of refractories in the aluminum, glass and chemical industries

Research Tasks

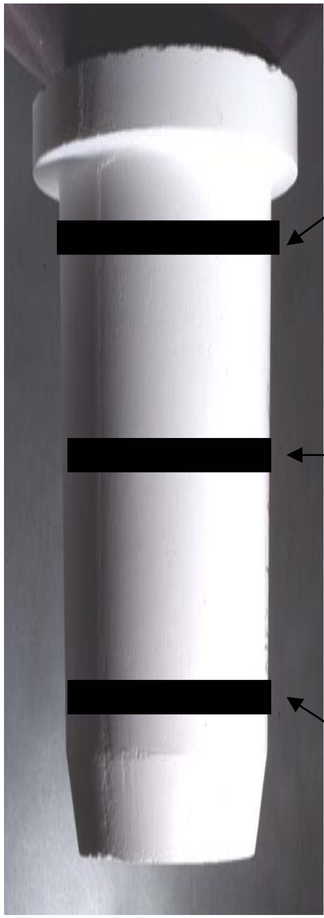
ORNL

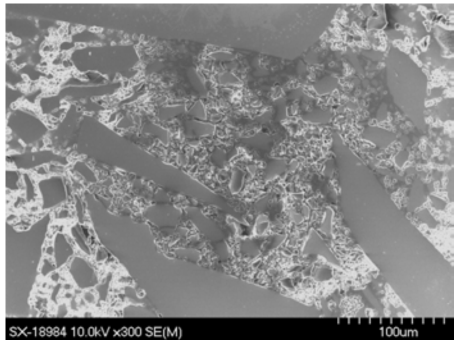
- Characterization of the porosity in delivery tubes
- Develop and optimize the surface modification process to close the porosity
- Develop high temperature glazes to seal the porosity of the refractory
- Examine the compatibility of the glazes with molten aluminum alloys

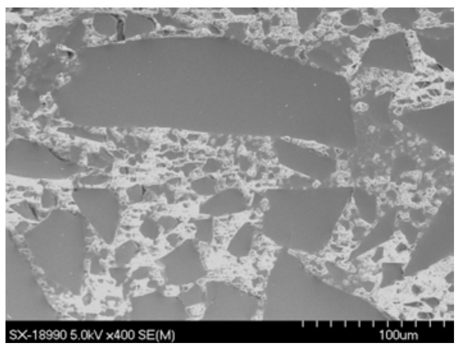
UMR

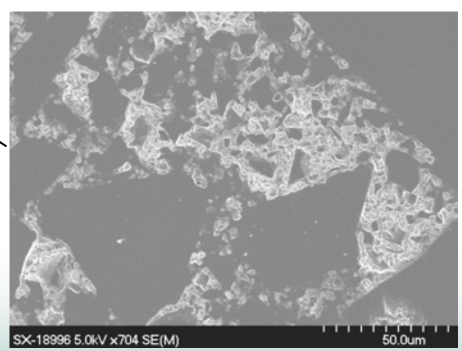
- Evaluate the permeability of as-received manufactured material utilizing a special designed permeameter at UMR
- Determine current particle size distribution of aggregate and optimize to obtain a continuous distribution to minimize permeability in castable formulations
- Evaluate the compatibility of the molten metal with the refractory and its wetting characteristics in both DFS and castable samples

Microstructural Characterization of the Slip Cast DFS Tubes

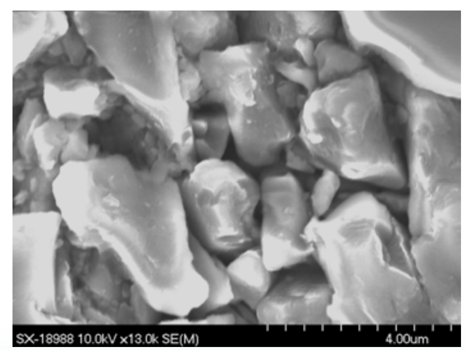








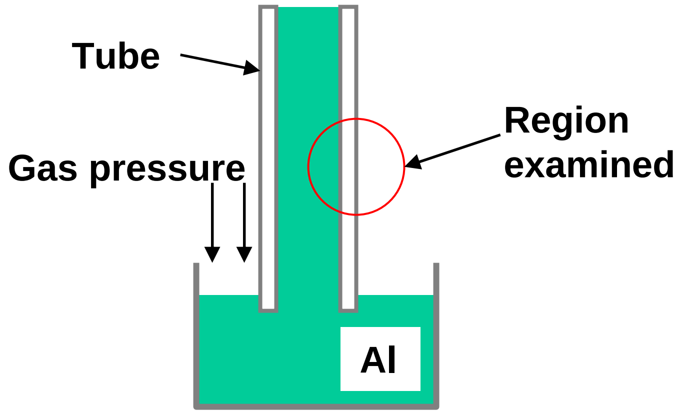
- No visual variation in the microstructure among the 3 sections
- 65% area fraction of dense SiO_2 particles
- 35% area fraction
  - Loosely packed small particles ranging from 5 μm on down in size

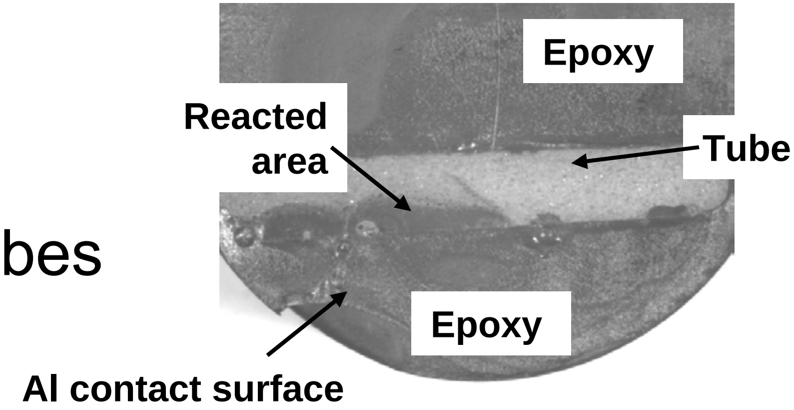


High magnification image of the matrix

Examination of Tubes which Reacted with Molten Aluminum

- Densified fused silica tubes
- Examined after use in Al-casting
- Reaction zones were found
  - Discrete points of initiation
  - Half-spherical shape
  - Dark gray color
- Approximately 10% of interior surface appeared to react
- No reaction zone penetrated through the thickness of the tubes that were examined

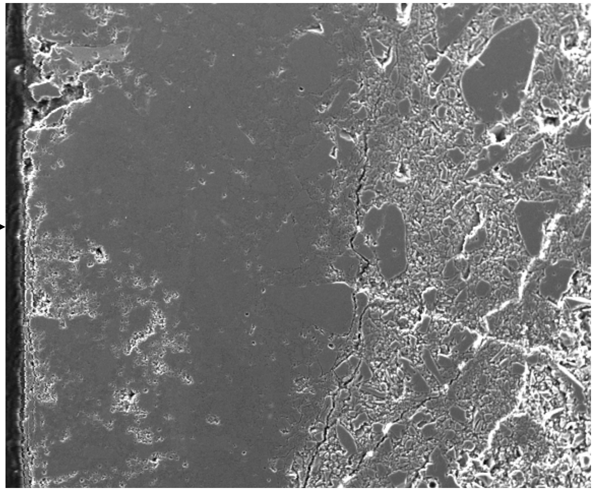




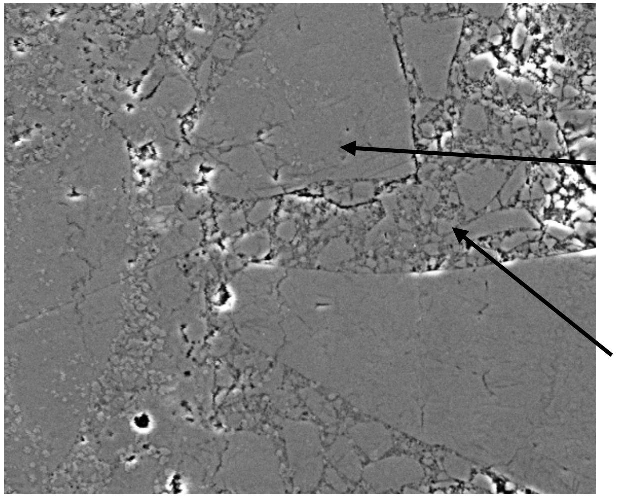
Reaction Zone Morphology

- Reaction zones were examined by SEM
- Morphology of grains did not change within the reaction zone

Tube Section After Use

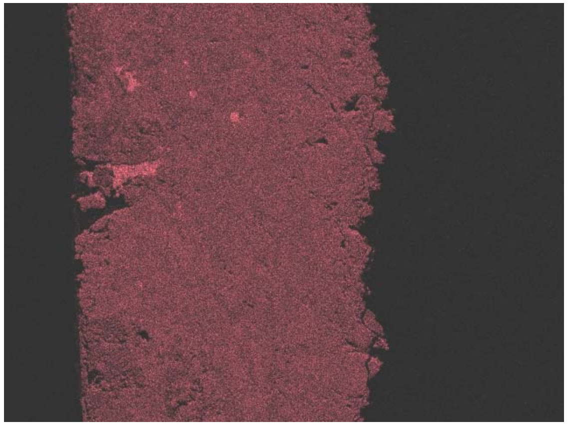


Reaction Zone

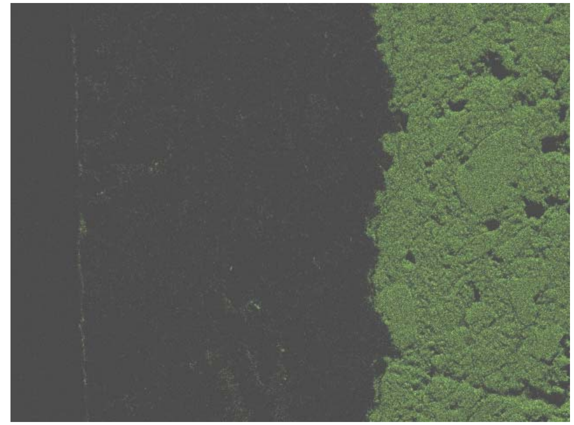


X-ray Mapping of Reaction Zone

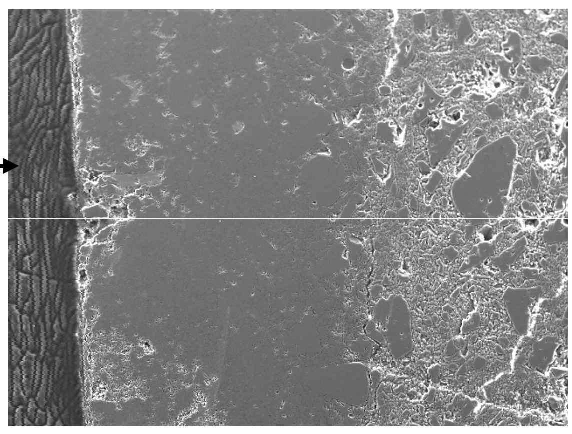
Al Map



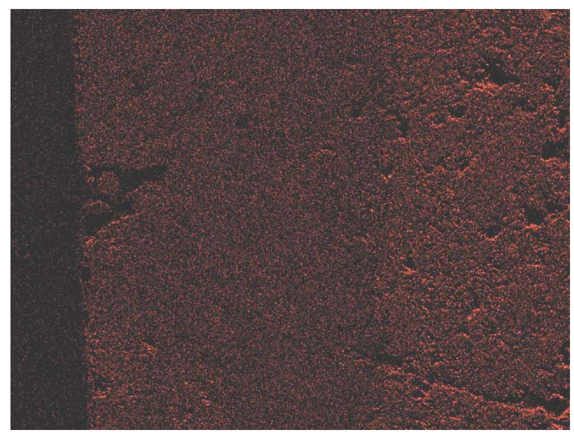
Si Map



SEM Image



O Map



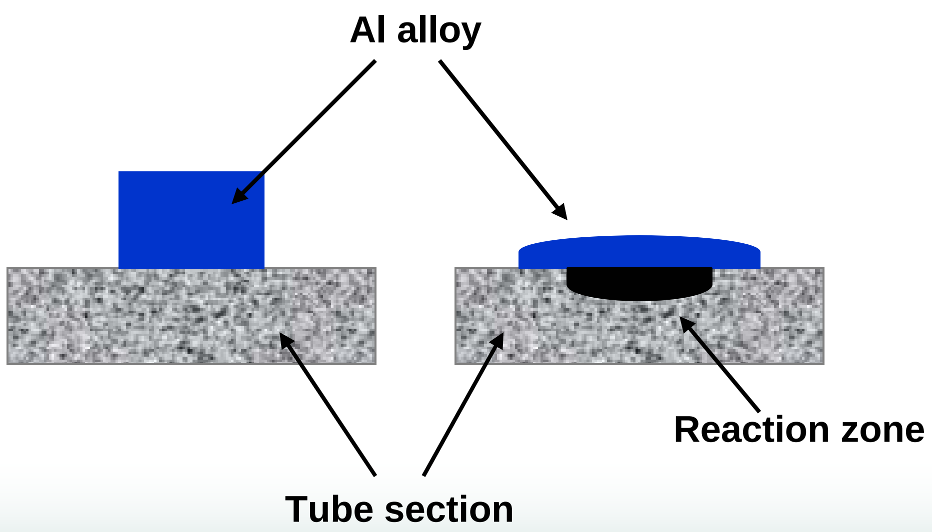
X-ray Mapping of Reaction Zone

- Reaction zone is enriched in Al
- Si is almost completely removed from reaction zone
- O is depleted, but not removed from reaction zone
- XRD confirms the presence of Al and Al_2O_3 in reaction zone
- Reaction is thermodynamically favorable

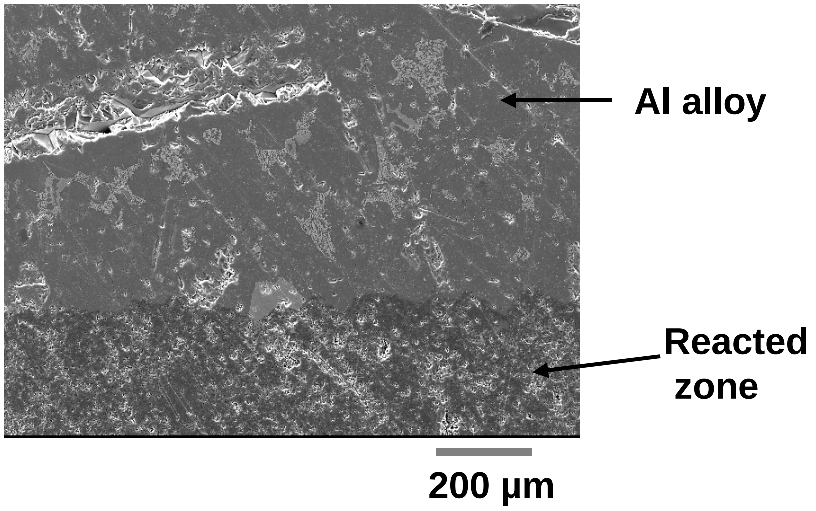
  ΔG_{rxn} = -544 kJ at 700°C

Wetting and Reaction Studies

- Replication of reaction under experimental conditions
  - Flowing argon (inert atmosphere)
  - 356 Al alloy placed on tube section
  - 1200°C for 1 hour
  - Produces comparable reaction



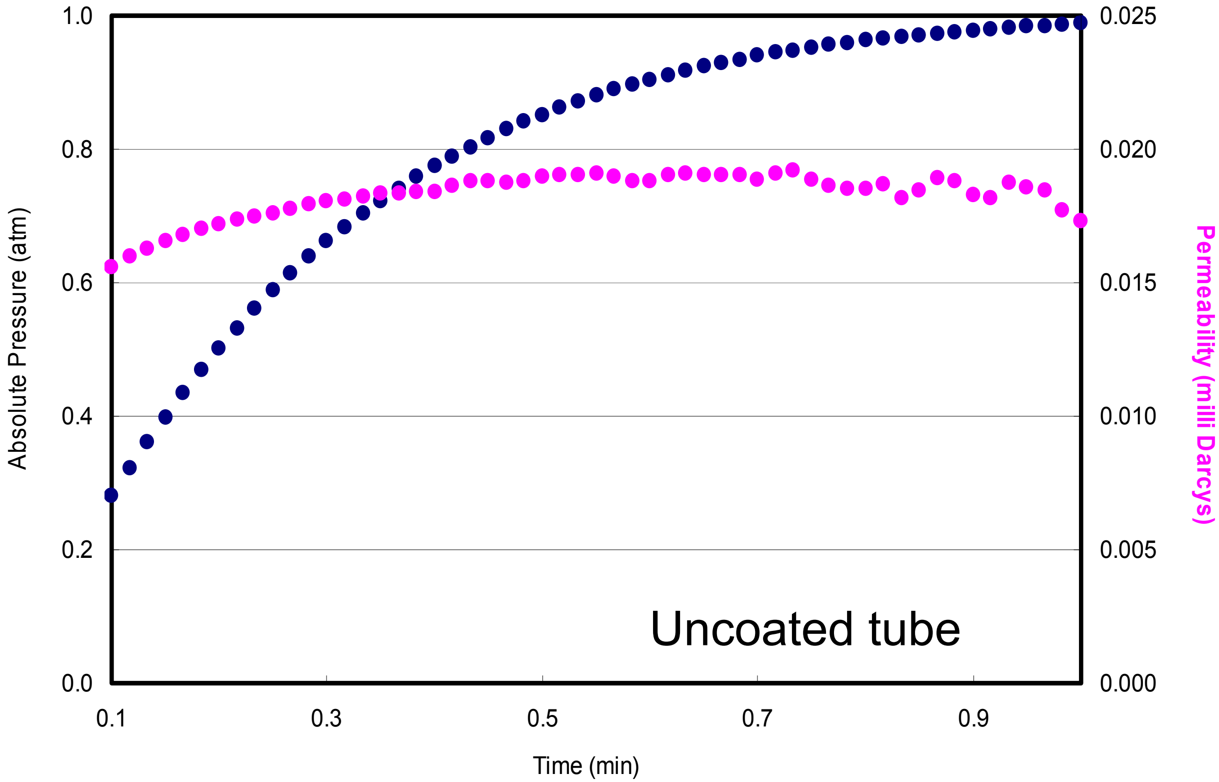
SEM micrograph



Permeability Measurement

- Full scale permeameter capable of measuring permeability of the full scale tube has been developed
- Formula developed to measure permeability
  - Assumptions
    - System obeys Darcy's Law
    - Constant thickness cylinder

Pressure Decay Data



$$K = \frac{\eta \, \ln\left(R_o / R_i\right) Q}{2 \, \pi \, L \, \Delta P}$$

η = fluid viscosity

R_o = tube outer radius

R_i = tube inner radius

Q = volume flow rate

L = tube length

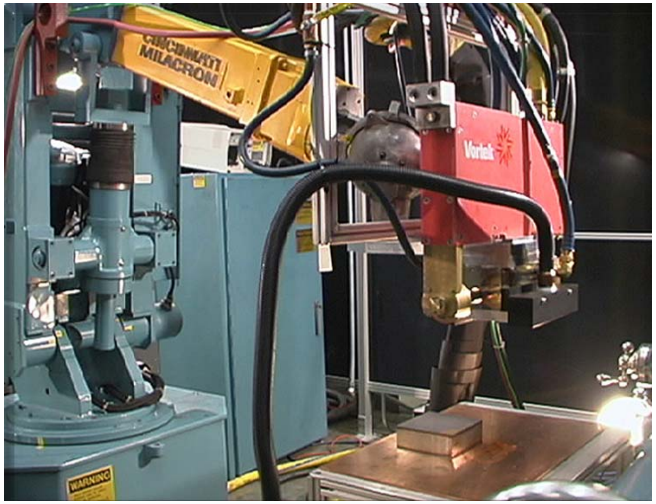
ΔP = differential pressure across tube wall

Q is determined from dP/dt and the system volume

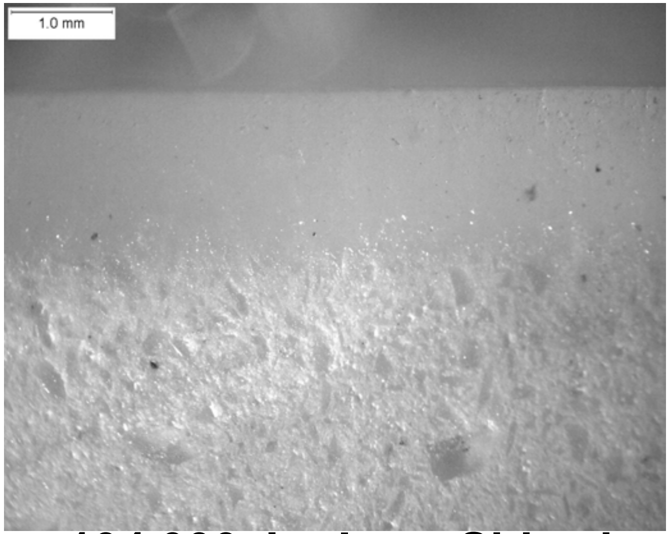
- Permeability is constant
- Previously coated tubes have shown a 67% improvement in permeability

High Density Infrared Plasma Arc Lamp Processing

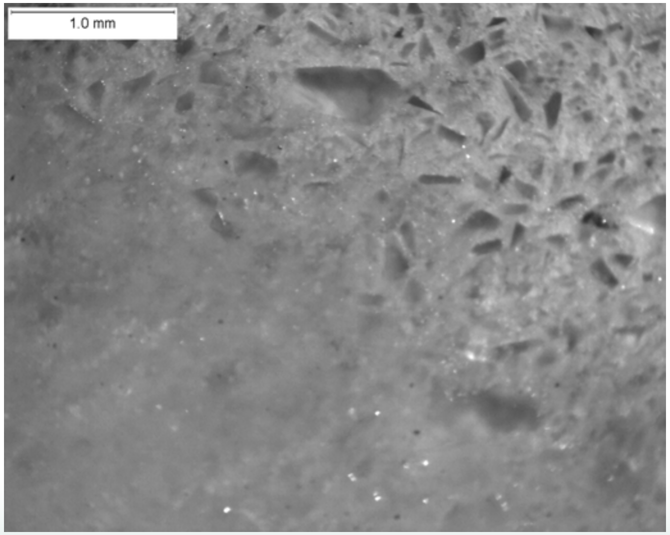
- Samples treated with HDI under varying processing conditions
- HDI Plasma melted the surface of the specimens forming a dense layer of SiO_2
- Tailor the melt zone depth with the amperage and time exposure
  - Decrease current and increase time – more uniform melt zone



Melt Zone Depth

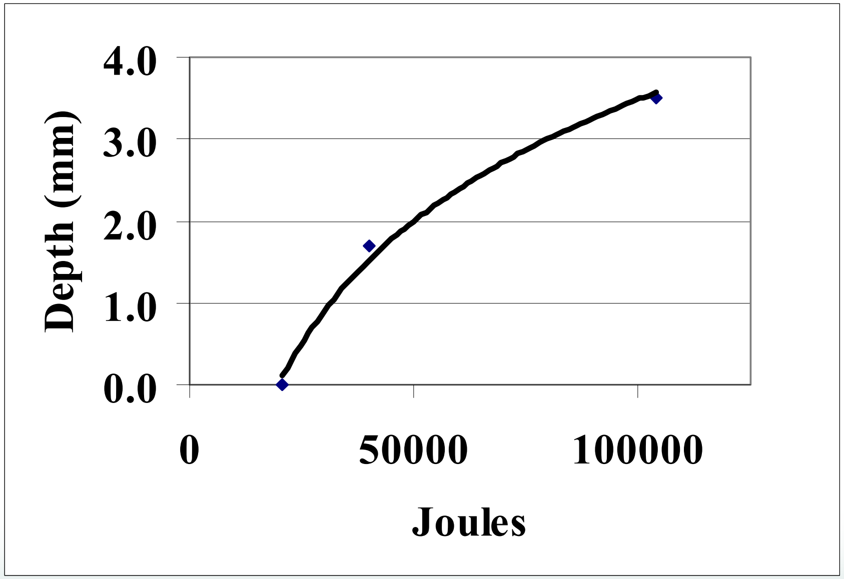


104,000 Joules – Side view

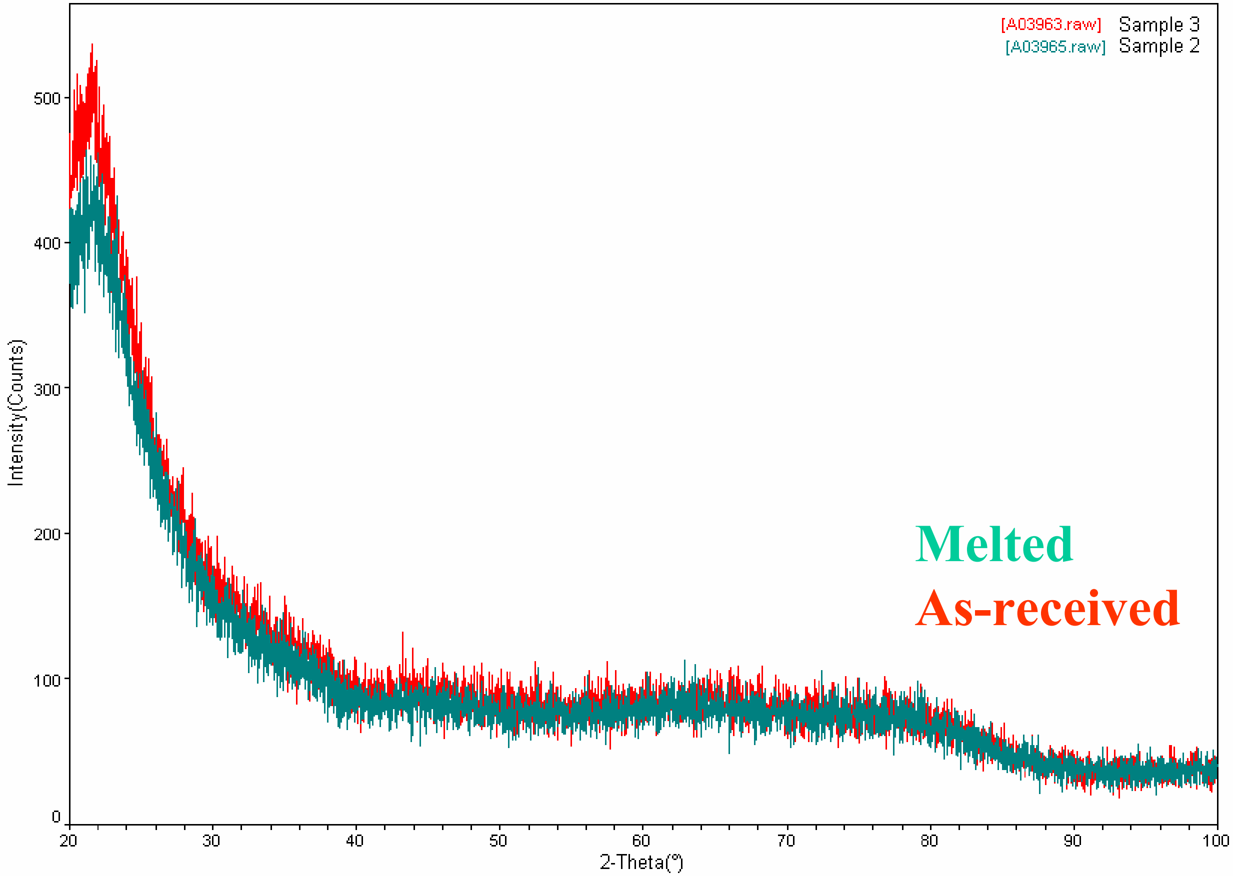


40,000 Joules – Top view

Joules	Melt Zone Depth (mm)
20,800	0.01
40,000	1.7
104,000	3.5



X-ray Diffraction of Melted Zone



Maintain the amorphous structure after processing the surface with the plasma arc lamp

Glazes

- Commercially available glazes(generally oxide glazes) have coefficient thermal expansions much greater than fused SiO_2 ($0.5 \times 10^{-6}/{}^{\circ}C$)
  - Higher CTE glaze can undergo spallation during heating
  - Difficult to obtain an amorphous glaze to match
  - Semicrystalline glazes

- Semicrystalline Glazes
  - Structure consists of low thermal expansion crystalline phases in a glassy matrix
  - Thermal expansion of semicrystalline (glass-ceramic) materials can be tailored depending on the crystalline phases present
  - Crystalline phases present are attributed to the thermal history

Selection of glazes

- Identified 8 glazes from literature
  - Selected these 4 based on:
    - Low CTE
    - Low reactivity with molten aluminum
    - (Oxide Weight %)

Oxide	(1)	(6)	(7)	(8)
Al_2O_3	29.2	23.19	11.29	14.79
B_2O_3	5	---	---	---
CaO	---	3.05	4.56	5.96
K_2O	5	---	---	---
Li_2O	11.3	4.53	3.31	4.34
MgO	---	6.58	3.27	4.28
SiO_2	49.5	62.65	47.48	53.83
ZnO	---	---	30.9	16
CTE	-0.9	1.3	0.34	0.36

CTE from literature

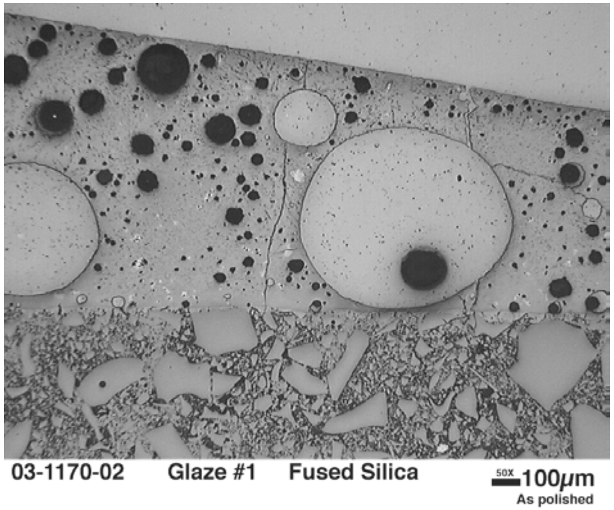
Firing and Heat Treatment

Glaze	Firing Schedule °C/h	Heat Treatment Schedule °C/h	Heating Rate	Crystalline Phases Expected	ΔGrxn (kJ @ 700°C)
1	1094/0.25	788/0.50	20 °C/min	β-spodumene ss	-142
6	1500/4	850/5 1050/3	3 °C/min 3 °C/min	β-spodumene ss, β-eucryptite ss, clinopyroxene	-142 -72 ---
7	1450/3.5	660/4 900/3	3 °C/min 3 °C/min	β-spodumene ss, β-eucryptite ss, Willemite	-142 -72 -416
8	1450/3	660/4 780/3	3 °C/min 3 °C/min	β-eucryptite ss, Willemite Diopside	-72 -416 ---

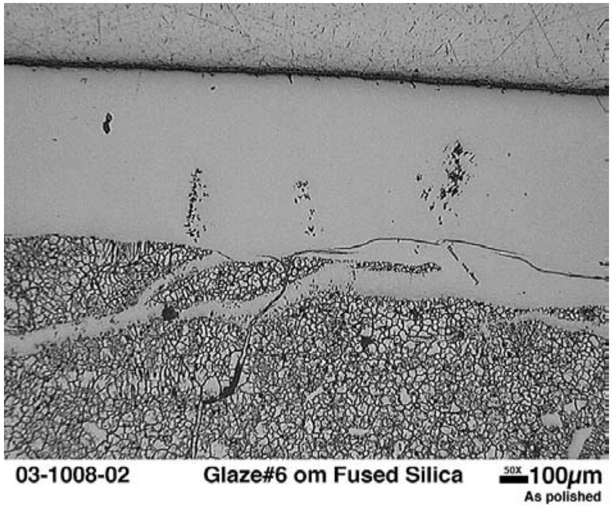
•ΔGrxn = -544 kJ at 700°C for the reaction of fused silica and molten Al

Optical Micrographs

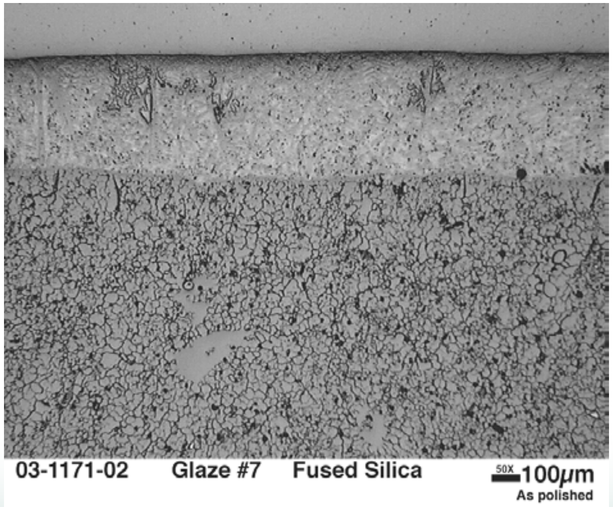
Glaze 1



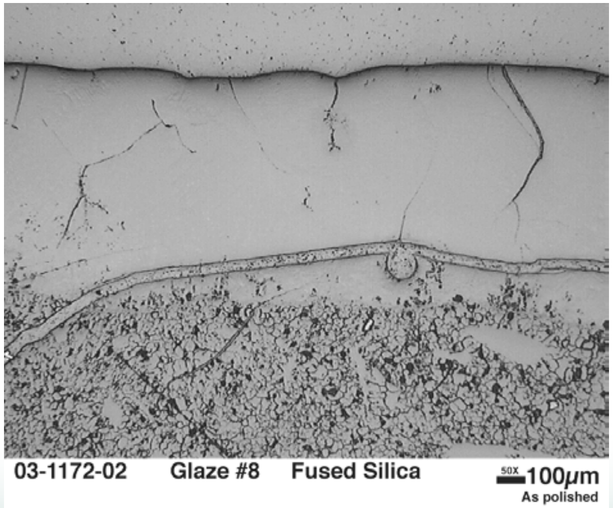
Glaze 6



Glaze 7

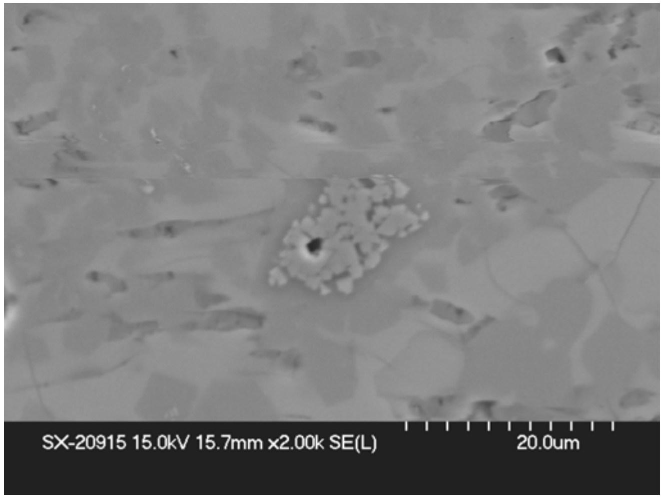


Glaze 8

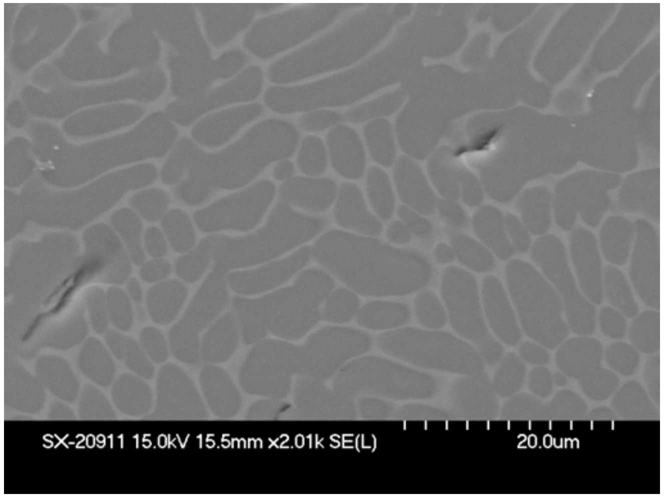


Higher Magnification Images of Glazes

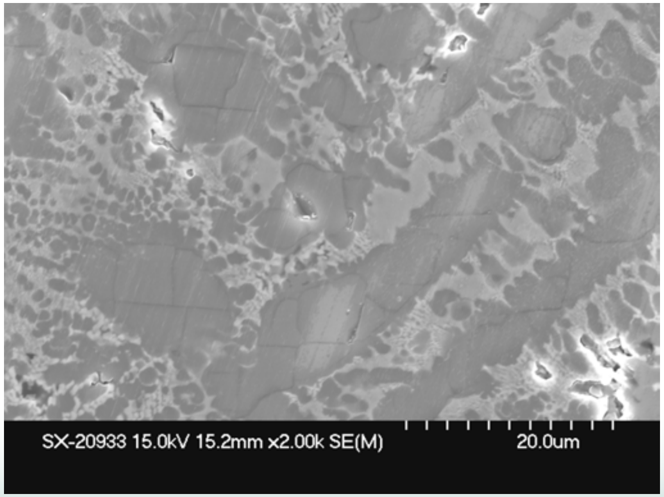
Glaze 1



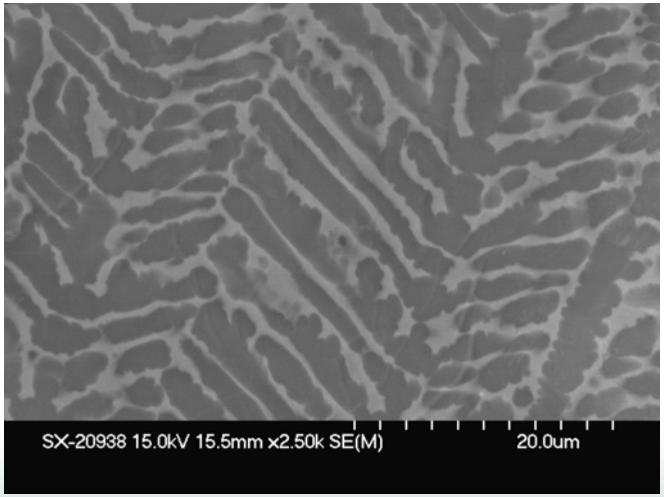
Glaze 6



Glaze 7



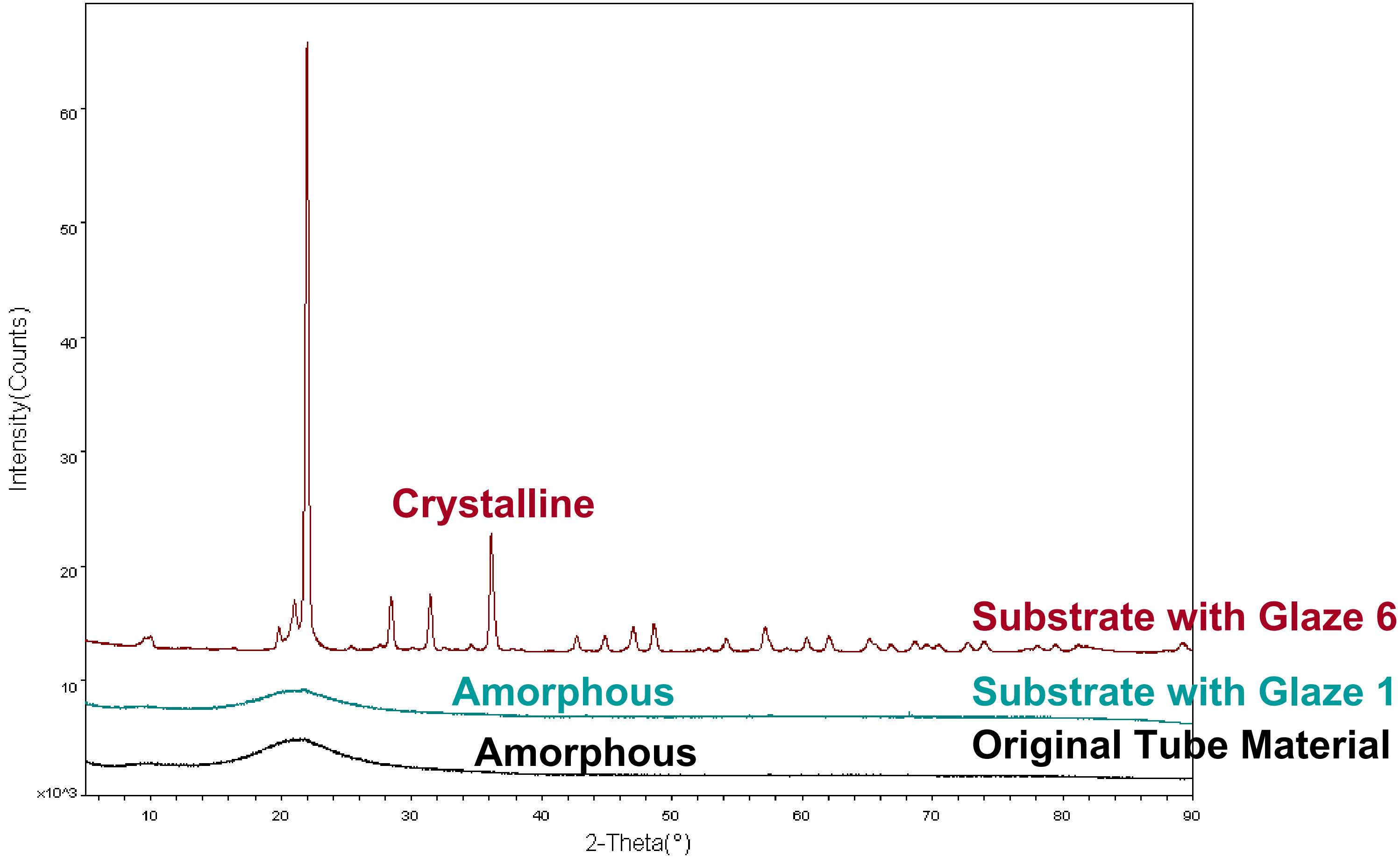
Glaze 8



Glazes

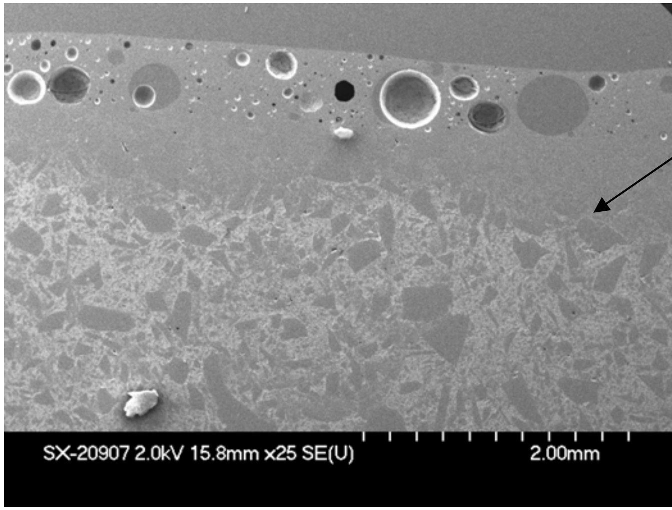
- All glazes seem to be adherent to fused silica
- X-ray show the crystalline structure of the glazes
- Thermal cycling of glazes
  - Any significant CTE mismatch would have been immediately obvious
  - Glazed samples were subjected to 2 heating cycles
  - Heat up to 700°C @ 100 °C/min
  - Held at 700 °C for 10 minutes
  - Cool to room temperature at the same rate
  - Preliminary results show that all 4 glazes are still adherent to fused silica
  - No spalling or cracks observed

X-ray Phase Analysis of Substrates with Glazes

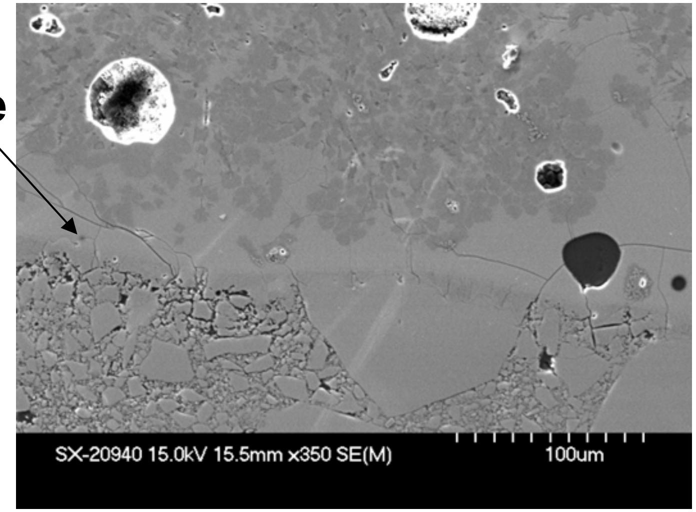


- Due to higher heating temperatures and times for glazes 6, 7, and 8
  - Crystalline cristobalite was formed in the fused silica substrate, which is undesirable due to the large change in volume

SEM Micrographs (Glaze 1)

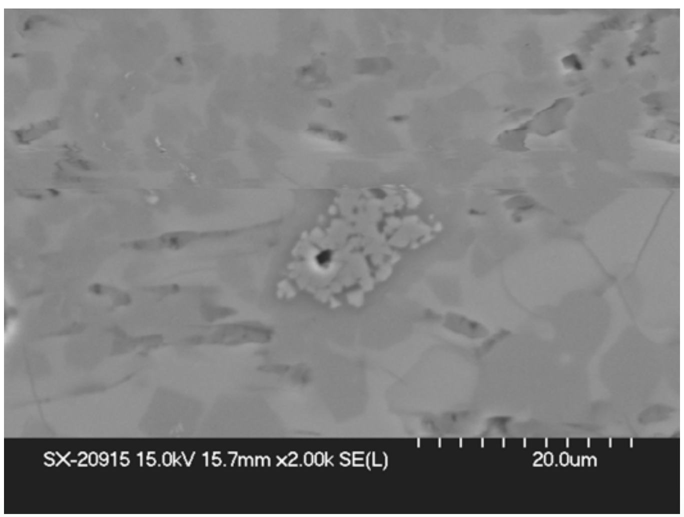


Interface

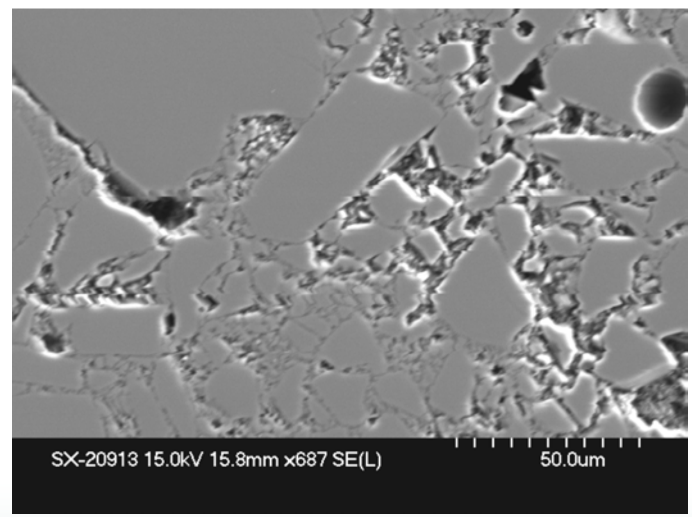


Interface – low mag

Interface – high mag



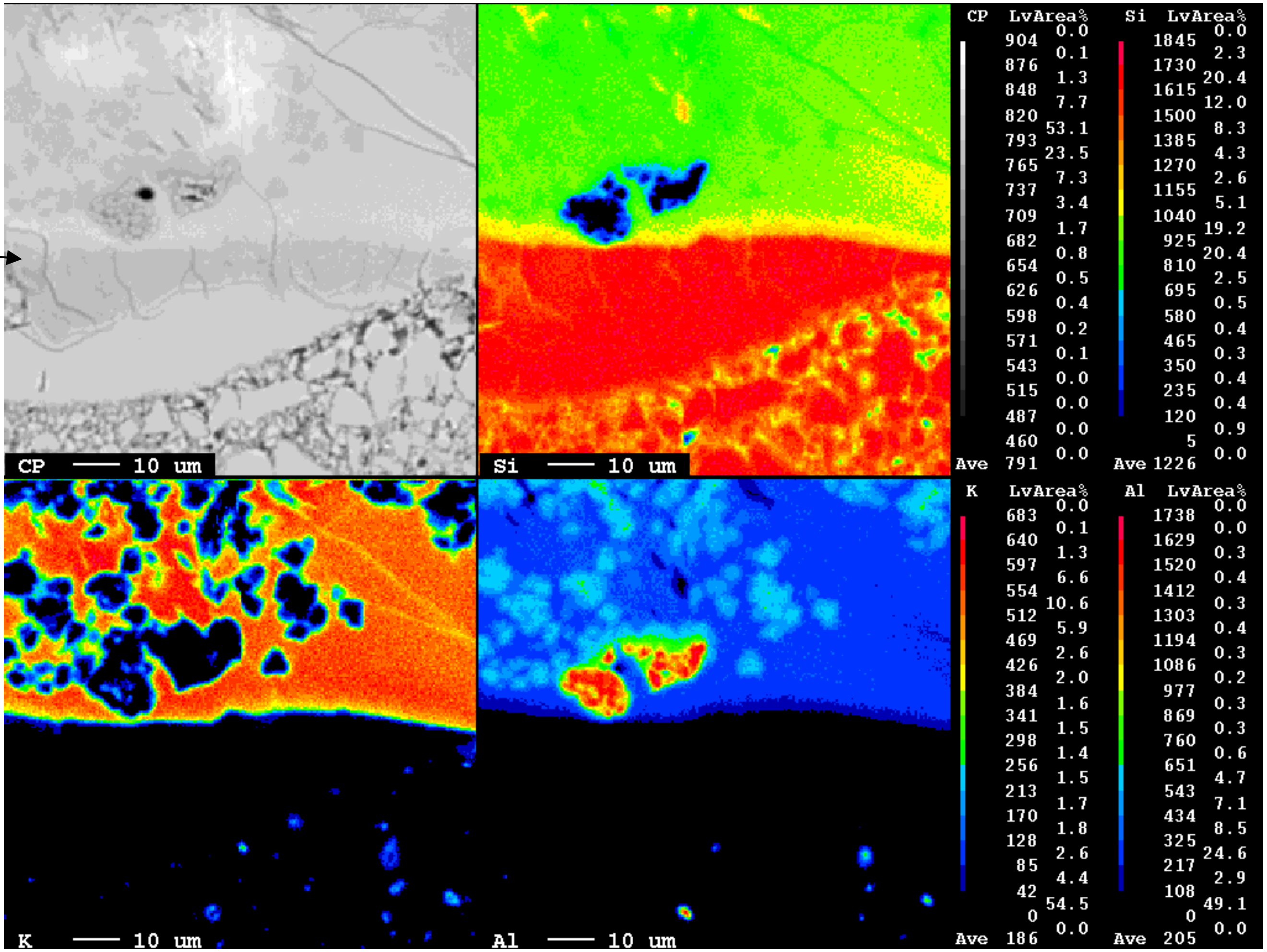
Glaze



Fused Silica

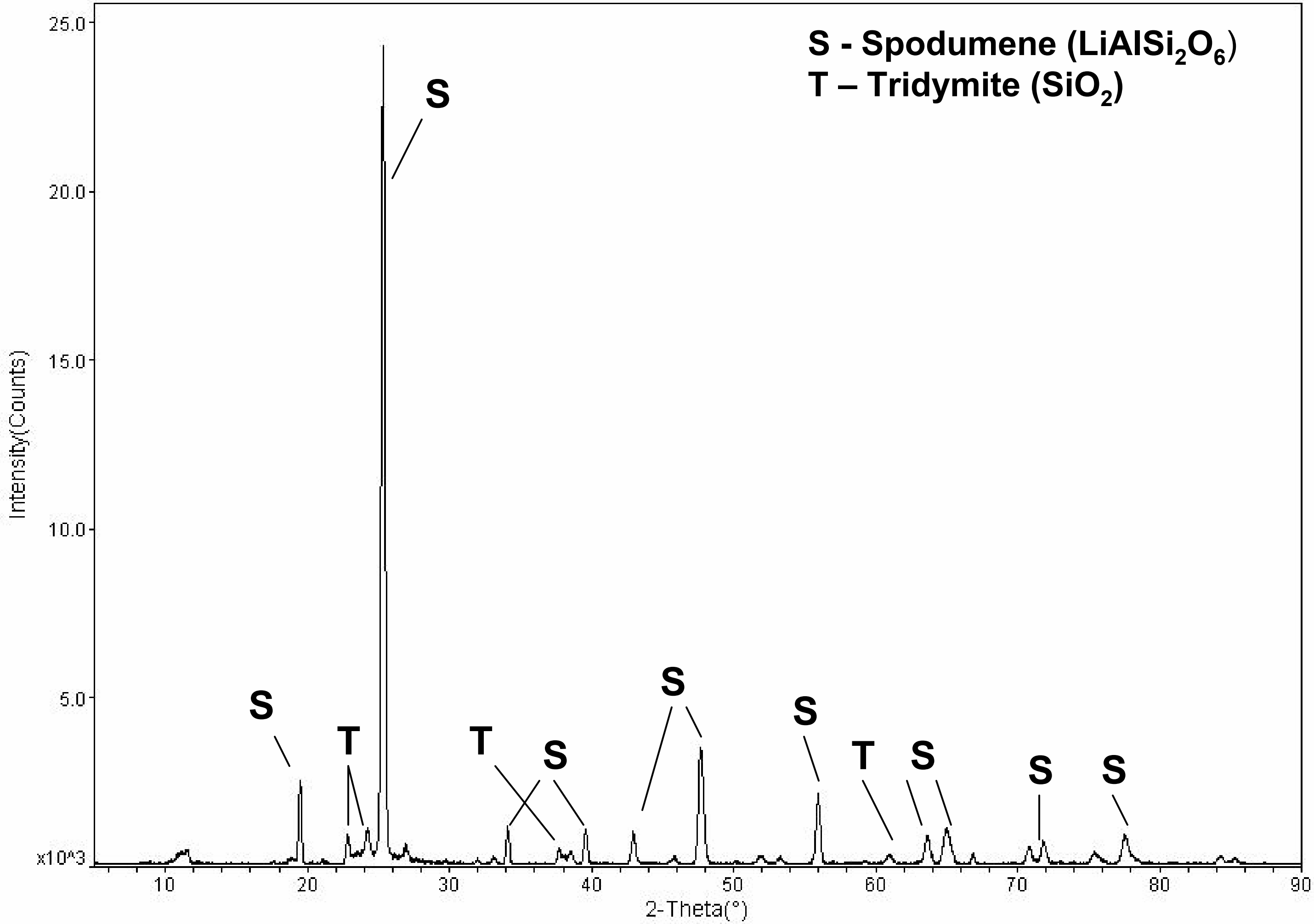
X-ray Mapping (Glaze 1)

Interface

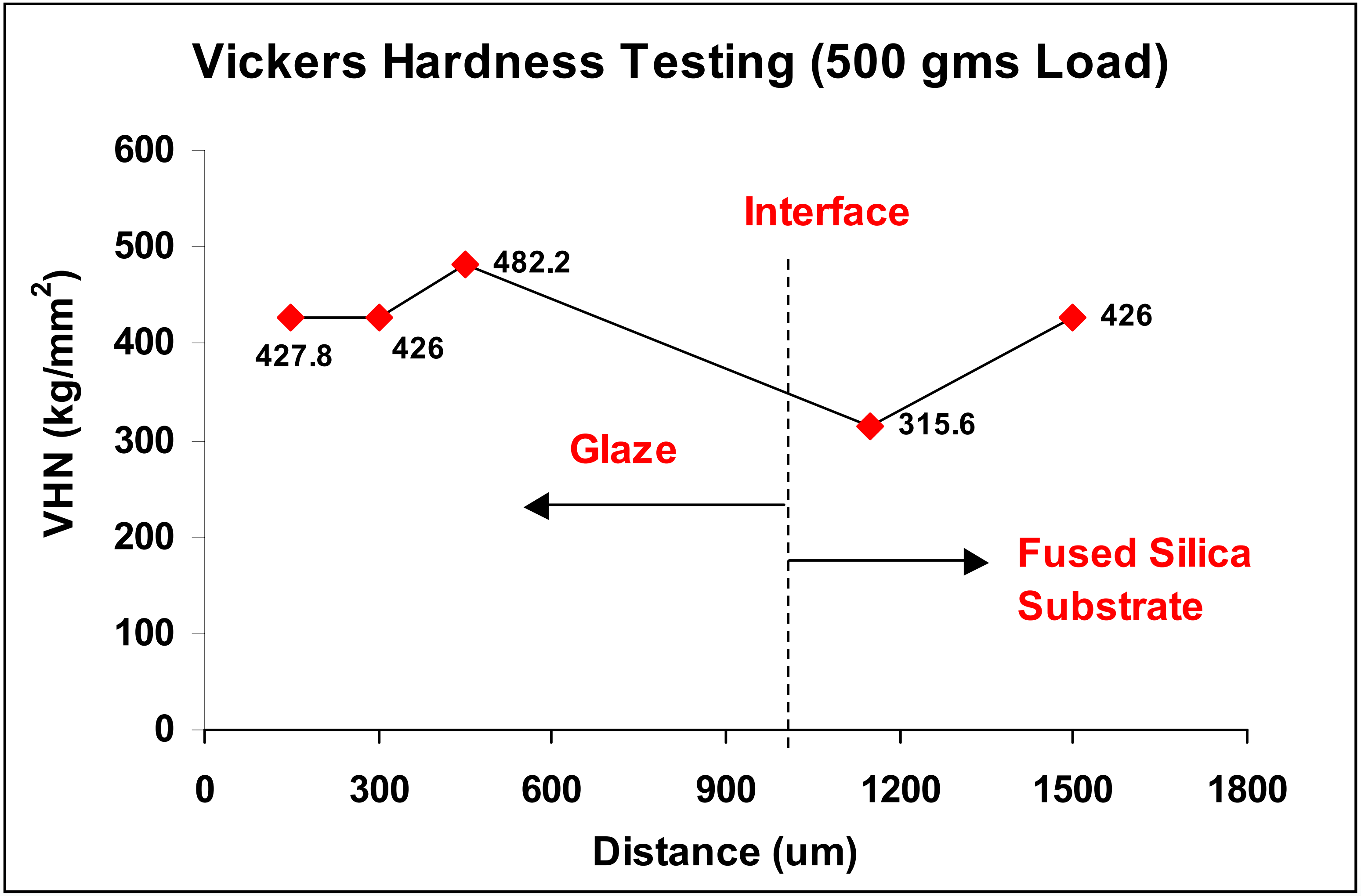


Glaze material does not diffuse into the substrate – maybe some K

X-ray Phase Analysis (Glaze 1)



Microhardness (Glaze 1)



Particle Size Distribution for Optimal Particle Packing - Castable Tubes

- 90% fused silica, ~5% fine alumina, ~5% cement, ~4-5% non-wetting agent
- Different particle size distributions are used in fabricating ceramics
  - Monosized – yields ~60% dense
  - Bi-modal – yields ~85% dense
  - Tri-modal – yields ~90% dense
  - Continuous (Funk and Dinger and Andreasen models)
    - Potential to achieve near full density distributions

$$CVPFT = \frac{D^n - D_s^n}{D_l^n - D_s^n}$$

(after Funk and Dinger)

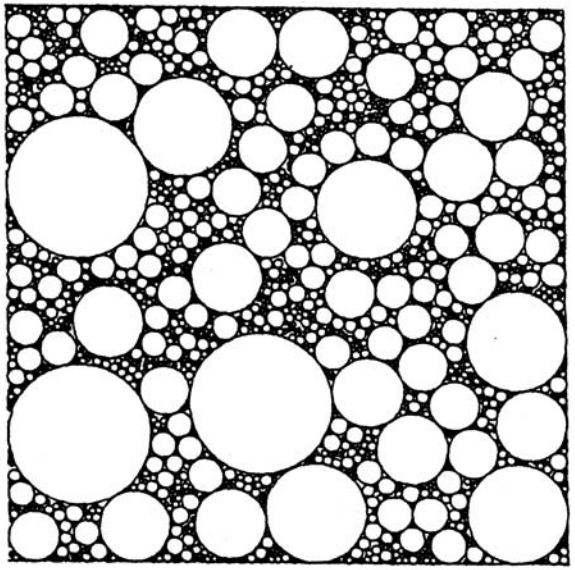
Three Parameter Continuous PSD

n: distribution modulus
typically chosen 0 < n < 1
larger values…coarser design
n=0.37 for theoretical maximum density

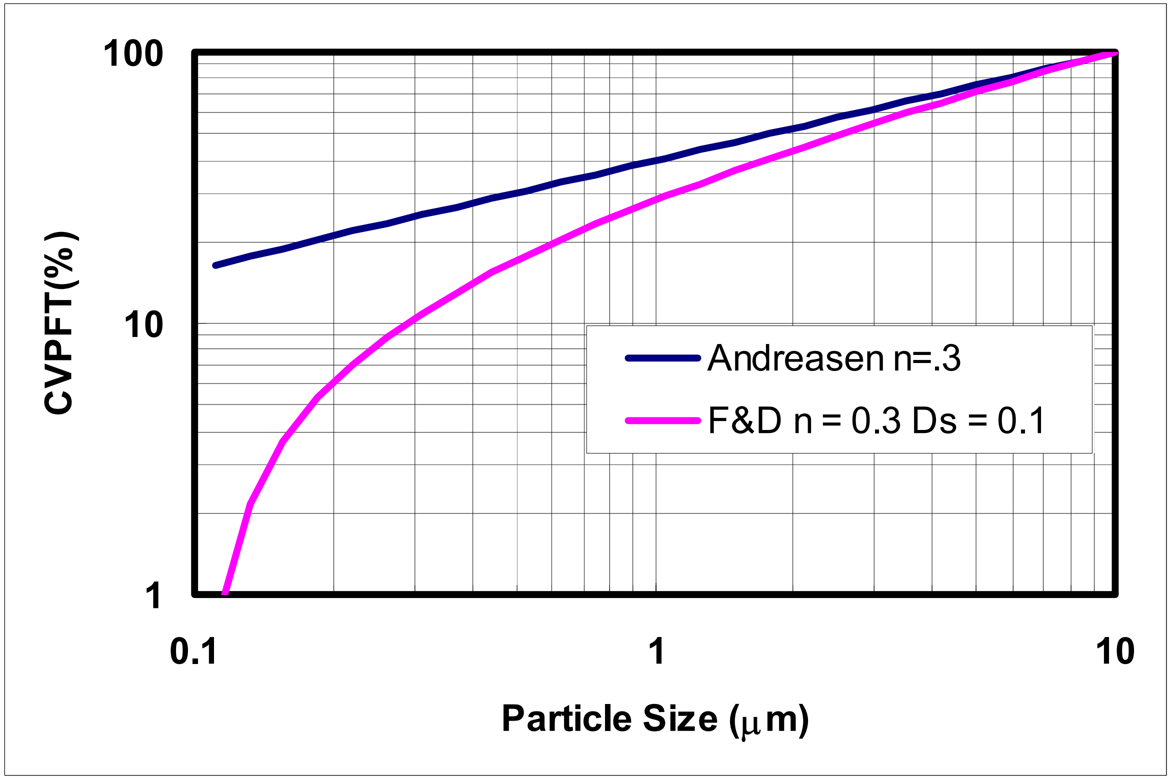
D_s: smallest particle size considered

D_l: largest particle size considered

Particle Size Distribution (Castable)



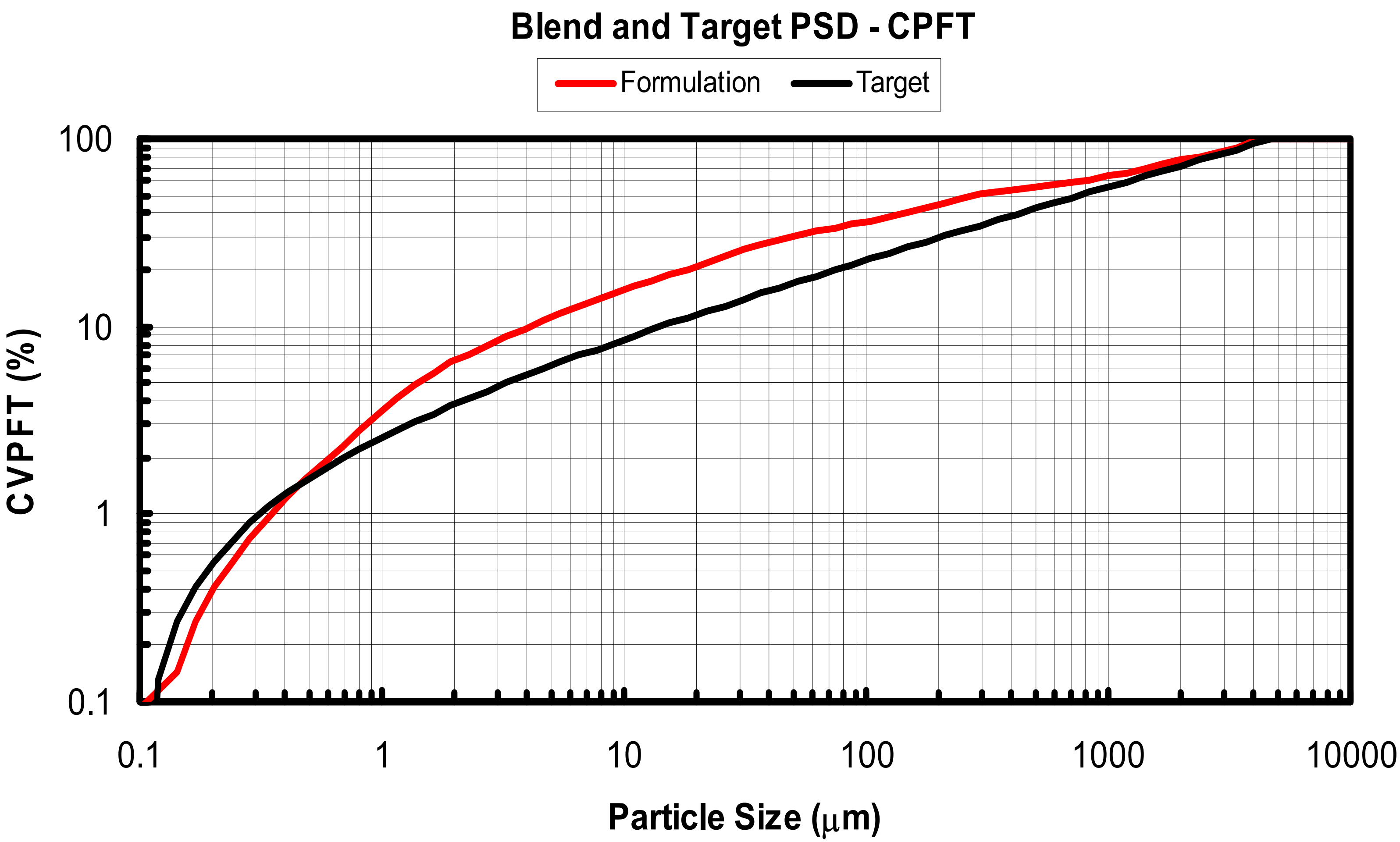
Computer model for selection of optimum aggregate to minimize permeability



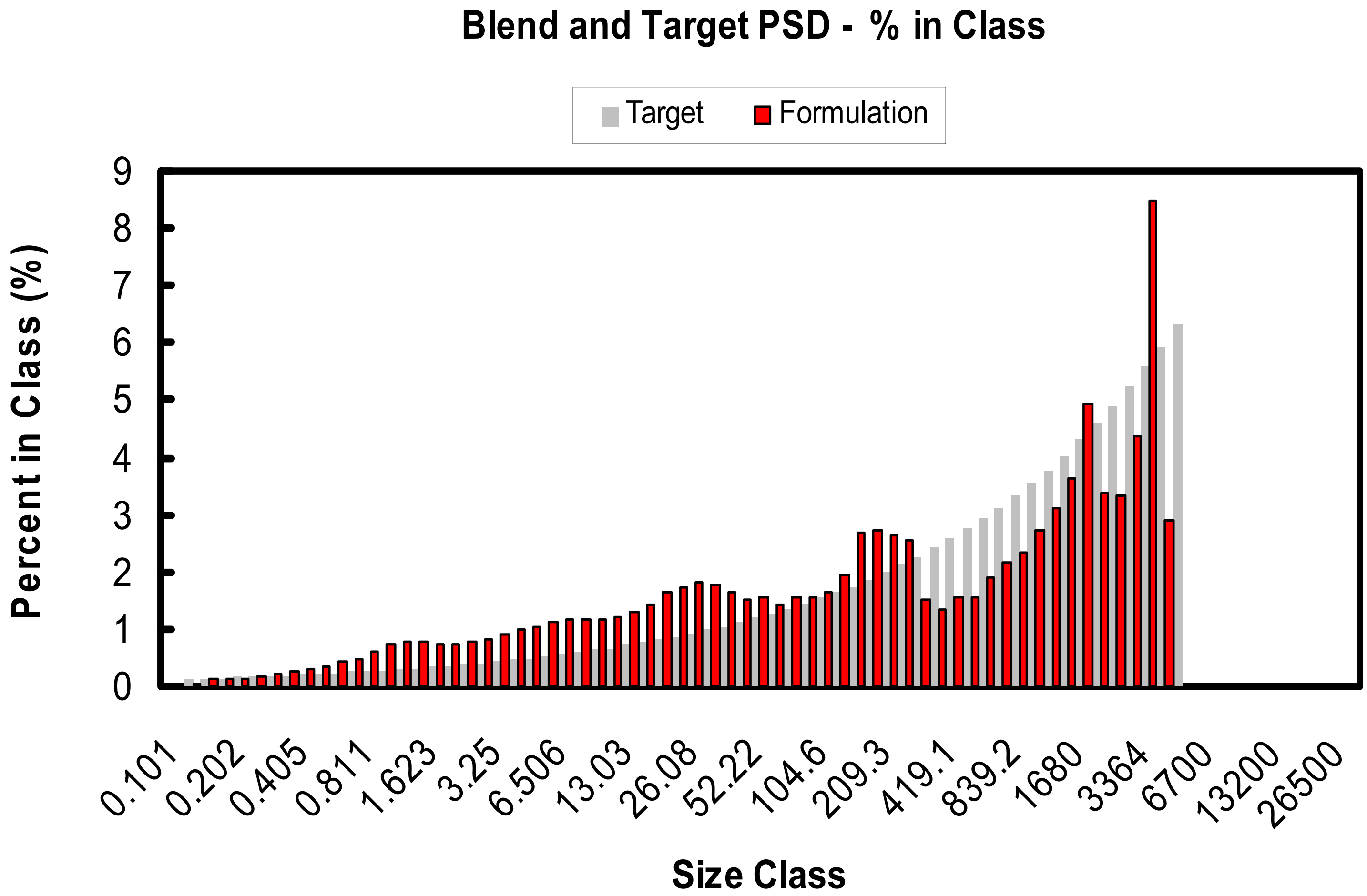
Castable Formulations

- High Density / Low Water Demand Castables
  - Optimize particle size using continuous distribution
- Required Data for Each Component
  - Particle size distribution
    - All sieves in series is optimal for aggregates
    - Laser or other similar technique for fine particles
  - Theoretical density and surface area
  - Complete chemistry
- Experience / Equipment Based Constraints
  - Batch size range
  - Desired overall chemistry
  - Cement content
  - Additive content
  - Top particle size

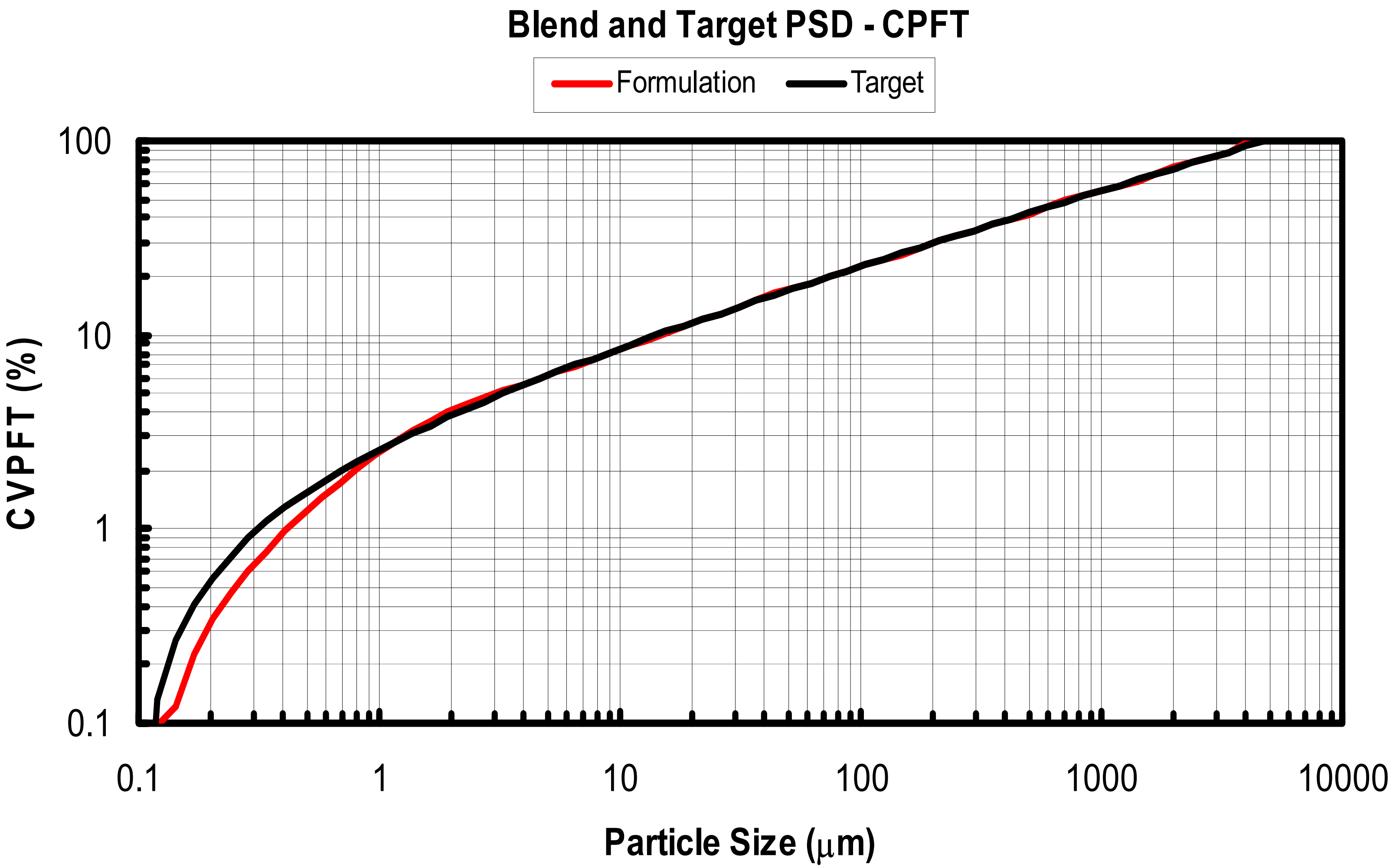
Initial Formulation vs. Target PSD



Deviation Within Each Size Class

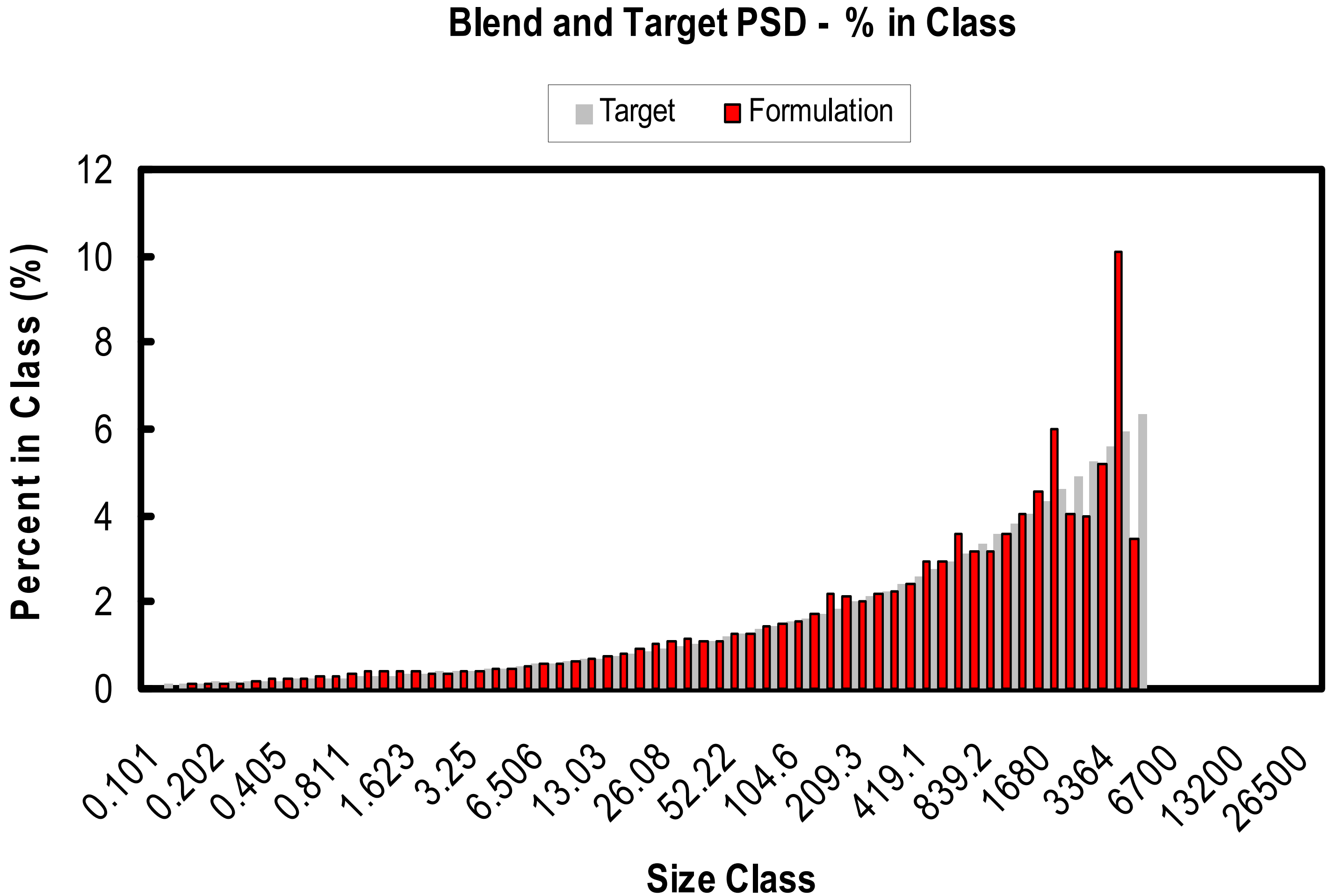


Formulation – No Constraints



Must be cautious of results – might propose impractical solution

Unconstrained Formulation – Size Class Deviation



Near Term Future Work / Milestones

- Glazes – Dense Fused Silica
  - Monolithic samples of the glazes to measure CTE
  - Glazes on fired and green state specimens
    - Fired under tube firing schedules (1160°C for 3.5 hrs)
    - Side by side comparison of the glaze on the fired and the unfired specimens
      - Microscopic analysis, hardness and phase analysis
      - Wettability and reactivity of glaze with molten Al
      - Measure permeability
  - Iterative process: vary glaze content and firing schedule to tailor CTE and non-wetting characteristics
- Particle Size Distribution – Castable Formulations
  - Optimize Castable Formulations
  - Evaluate Formulations
    - Water demand
    - Density / Porosity
    - Permeability
    - Strength

Near Term Future Work / Milestones

- Extend laboratory results to field
  - Applying the suitable glaze to a full scale tube
  - Permeability of the glazed tube
  - Wetting and reactivity with Al
  - Testing in Industrial Partner's facility
- Apply findings to other areas
  - Optimize particle size distribution of refractories used in other areas of primary and secondary aluminum facilities
  - Identify glazes for application to refractory components with different CTE's